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| (51) International Patent Classification ⁴ : C08J 9/32, C08L 63/00 H01Q 15/14, C08K 7/00 | | A1 | (11) International Publication Number: WO 85/05113 (43) International Publication Date: 21 November 1985 (21.11.85) |
| <p>(21) International Application Number: PCT/US85/00625</p> <p>(22) International Filing Date: 9 April 1985 (09.04.85)</p> <p>(31) Priority Application Numbers: 607,847 609,178</p> <p>(32) Priority Dates: 7 May 1984 (07.05.84) 11 May 1984 (11.05.84)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: HUGHES AIRCRAFT COMPANY [US/ US]; 200 North Sepulveda Boulevard, El Segundo, CA 90245 (US).</p> <p>(72) Inventors: DuPONT, Preston, S. ; 9046 Bertrand Avenue, Northridge, CA 91325 (US). FREEMAN, Janet, E. ; 129 North Bonnie Avenue #1, Pasadena, CA 91106 (US). RITTER, Robert, E. ; 741 Cloyd Road, Palos Verdes Estates, CA 90274 (US). WITTMANN, Alois ; 29017 Geronimo Drive, Palos Verdes, CA 90274 (US). OLDHAM, Susan, L.; 3472 Heather Road, Long Beach, CA 90808 (US).</p> | | <p>(74) Agents: LACHMAN, Mary, E. et al.; Hughes Aircraft Company, Post Office Box 1042, Bldg. C2, M.S. A126, El Segundo, CA 90245 (US).</p> <p>(81) Designated States: AU, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, SE (European patent).</p> <p>Published <i>With international search report.</i></p> | |
| <p>(54) Title: FIBER-REINFORCED SYNTACTIC FOAM COMPOSITES AND METHOD OF FORMING SAME</p> <p>(57) Abstract</p> <p>Fiber-reinforced syntactic foam composites having a low specific gravity and a low coefficient of thermal expansion suitable for forming lightweight structures for spacecraft applications are prepared from a mixture of a heat curable thermosetting resin, hollow microspheres having a diameter of about 5 to 200 micrometers and fibers having a length less than or equal to 250 micrometers.</p> | | | |

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-1-

FIBER-REINFORCED SYNTACTIC
FOAM COMPOSITES
AND METHOD OF FORMING SAME

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates, in general, to
5 syntactic foam composites and, more particularly, to
fiber-reinforced thermosetting resin based syntactic
foam composites exhibiting a low specific gravity and
a low coefficient of thermal expansion.

10 2. Description of the Prior Art

A continuing objective in the development of
satellites is to optimize satellite payload weight.
One means of achieving this objective is to reduce the
intrinsic weight of various operational elements within
15 the spacecraft. It has been recognized by the art that
the desired weight reduction could be realized by
replacing conventional materials, such as aluminum,
with lower density synthetic composites possessing
requisite mechanical, thermal and chemical stability.
20 Included in these low density synthetic composites is a
group of materials referred to in the art as syntactic
foams.

1 Syntactic foams are produced by dispersing
microscopic rigid, hollow or solid particles in a
liquid or semi-liquid thermosetting resin and then
hardening the system by curing. The particles are
5 generally spheres or microballoons of carbon, polystyrene,
phenolic resin, urea-formaldehyde resin, glass, or
silica, ranging from 20 to 200 micrometers in diameter.
Commercial microspheres have specific gravities ranging
10 from 0.033 to 0.33 for hollow spheres and up to 2.3 for
solid glass spheres. The liquid resins used are the
usual resins used in molding reinforced articles, e.g.,
epoxy resin, polyesters, and urea-formaldehyde resins.

15 In order to form such foams, the resin containing
a curing agent therefor, and microspheres may be mixed
to form a paste which is then cast into the desired
shape and cured to form the foam. The latter method,
as well as other known methods for forming syntactic
foams, is described by Puterman et al in the publication
20 entitled "Syntactic Foams I. Preparation, Structure,
and Properties," in the Journal of Cellular Plastics,
July/August 1980, pages 223-229. When fabricated in
large-block form, such foams possess a compressive
strength which has made them suitable for use in submerged
structures. In addition, the more pliable versions of
25 the foam are utilized as filler materials which, after
hardening, function as a machinable, local-densification
substance in applications such as automobile repair and
the filling of structural honeycombs. Despite these
characteristics of adequate compressive strength, good
30 machineability, and light weight, such foams lack the
degree of dimensional and thermal stability required to
render them applicable for the spacecraft environment.
More specifically, syntactic foam systems tend to
exhibit varying filler orientation and distributions
35 within the geometrical areas in a molded intricate
structure, which limits the structural intricacy that

1 can be achieved, as well as reducing dimensional
stability. If syntactic foam systems are too highly
filled, sacrifices are made in moldability, coefficient
of thermal expansion, strength, density, dimensional
5 stability and stiffness. Moreover, such foams tend to
exhibit poor adhesion to metallic plating which is
required to form the desired product, such as an antenna
component.

10 In order for the syntactic foam to be useful
as a substitute for aluminum in antenna and antenna
microwave components in a spacecraft, the foam must
have the following characteristics.

15 (1) The material must have a specific gravity
of 1.00 or less, as compared to a specific gravity
of 2.7 for aluminum.

20 (2) The material must have a linear coefficient
of thermal expansion (α or CTE) comparable
to that of aluminum, preferably close to
 13×10^{-6} in/in/ $^{\circ}$ F (23×10^{-6} cm/cm/ $^{\circ}$ C) or less.
Thermal distortion of antenna components subjected
to thermal cycling in the extremes of the space
environment is a major contributing factor to
gain loss, pointing errors, and phase shifts.

25 (3) The material must meet the National
Aeronautics and Space Administration (NASA)
outgassing requirements to insure that the
material does not release gaseous component
substances which undesirably accumulate on other
spacecraft parts in the outer-space vacuum.

30 (4) The material must have long-term
stability, as required for parts exposed to the
space temperature environment (e.g., -100 $^{\circ}$ F to
250 $^{\circ}$ F or -73 $^{\circ}$ C to 121 $^{\circ}$ C) for extended periods of
time, such as 10 years.

1 (5) The material must be capable of being
cast into complex configurations in order to form
component parts for antenna structures, such as
waveguides or antenna feed distribution networks.

5 The art, until the present invention, has been
unable to satisfy these requirements and particularly the
requirement for a low coefficient of thermal expansion
(α). Thus, known epoxy resin based syntactic foams filled
with 10 to 30% by volume hollow microspheres generally
have a α in the range of 17 to 36×10^{-6} in/in/ $^{\circ}\text{F}$
10 (30 to 65×10^{-6} cm/cm/ $^{\circ}\text{C}$).

15 A need, unsatisfied by existing technology, has
thus developed for a syntactic foam material which is
both lightweight and of sufficient mechanical, thermal
and chemical stability to enable it to be substituted
for aluminum in physically demanding satellite
environments.

SUMMARY OF THE INVENTION

20 The unresolved needs of the art are satisfied by
the present invention which provides thermally stable
fiber-reinforced syntactic foam composites having a
specific gravity of less than 1.0 and a linear coefficient
of thermal expansion of about 25×10^{-6} in/in/ $^{\circ}\text{F}$
25 (45×10^{-6} cm/cm/ $^{\circ}\text{C}$) or less, which are prepared from
an admixture of a heat curable thermosetting resin,
hollow microspheres having a diameter between about 5
and about 200 micrometers and fibers having a length of
about 50 to about 250 micrometers.

30 The syntactic foam composites of the present
invention can be cast as complex structures which
contain lightweight hollow microspheres having fibers,
such as graphite fibers, in the voids between the
microspheres, with the microspheres and fibers being

1 bonded together by the heat cured resin matrix. The
composites of the present invention readily meet the
specific gravity, coefficient of thermal expansion and
NASA outgassing requirements, which easily qualify the
5 composites as aluminum substitutes for spacecraft use.

DETAILED DESCRIPTION OF THE INVENTION

In order to form the fiber-resin-microsphere composite of the present invention having the desired density and coefficient of thermal expansion, each of the three components must be selected so that the resulting combination thereof provides a mixture amenable to being cast into the desired configuration, as well as providing a final product having the required structural and physical properties. Acceptable mixtures must have a viscosity that produces an accurate, void-free casting with uniform material properties. In addition, the proportion of fiber in the composite must provide the required thermal expansion, strength, and stiffness properties. Further, the microsphere component must be chosen to provide the required low density in the composite. Finally, each of the components must be capable of being combined with the other components and the effect of each on the other in the mixture thereof, as well as in the final composite must be taken into account. In particular the properties of the composite are influenced by the properties, relative volume ratios, and interactions of the individual components. More specifically, density, strength, stiffness (brittleness), coefficient of thermal expansion and processibility are strong functions of filler and fiber type, volume ratios and micropacking. The following discussion provides a more detailed consideration of these various factors. It should be noted that in the

1 following discussion, the term "syntactic foam" is used
herein to denote a filled polymer made by dispersing
rigid, microscopic particles in a fluid polymer or
resin and then curing the resin, as is known in the
5 art. The term "fiber-reinforced syntactic foam composite"
is used herein to denote the cured product formed from
the mixture of resin, microballoons, and reinforcing
fibers in accordance with the present invention.

10 1. Heat Curable Resin

The heat curable, thermosetting resins used to
prepare the syntactic foam composites of the present
invention can be any heat curable thermosetting resin
having appropriate viscosity for casting (e.g., less
than 1000 centipoise), pot life (e.g., greater than 2
15 hours), coefficient of thermal expansion, and thermal
stability in the temperature range of -100°F to 250°F
(-73°C to 121°C) required in the space environment.
The resin material contains a curing agent which reacts
20 with the resin to produce a hardened material. Curing
agents and other additives will, of course affect the
viscosity and other properties of the final mixture
from which the composite is formed. Examples of suitable
resins include low viscosity, polymerizable liquid
25 polyester resins which comprise the product of the
reaction of at least one polymerizable ethylenically
unsaturated polycarboxylic acid, such as maleic acid or
its anhydride, and a polyhydric alcohol, such as, for
example, propylene glycol and optionally, one or more
30 saturated polycarboxylic acids, such as, for example,
phthalic acid or its anhydride. Other suitable resins
include condensates of formaldehyde such as urea-
formaldehyde, melamine-formaldehyde and phenol-
formaldehyde resins. Preferred resins for use in the

1 practice of the present invention are epoxy resins
having 1,2 epoxy groups or mixtures of such resins,
and include cycloaliphatic epoxy resins such as the
glycidyl ethers of polyphenols, liquid Bisphenol-A
5 diglycidyl ether epoxy resins (such as those sold
under the trademarks Epon 815, Epon 825, Epon 828 by
Shell Chemical Company), phenolformaldehyde novolac
polyglycidyl ether epoxy resins (such as those sold
under the trademarks DEN 431, DEN 438 and DEN 439 by
10 Dow Chemical Company), and epoxy cresol novolacs (such
as those sold under the trademarks ECN 1235, ECN 1273,
ECN 1280 and ECN 1299 by Ciba Products Company).

The particular epoxy resins preferred in the
practice of the present invention are polyglycidyl
15 aromatic amines, i.e. N-glycidyl amino compounds prepared
by reacting a halohydrin such as epichlorohydrin with
an amine. Examples of the most preferred polyglycidyl
aromatic amines include diglycidylaniline, diglycidyl
orthotolididine, tetraglycidyl ether of methylene dianiline
20 and tetraglycidyl metaxylene diamine, or mixtures
thereof.

The epoxy resins which are preferably in liquid
form at room temperature are admixed with polyfunctional
curing agents to provide heat curable epoxy resins
25 which are cross-linkable at a moderate temperature,
e.g., about 100°C, to form thermoset articles. Suitable
polyfunctional curing agents for epoxy resins include
aliphatic polyamines of which diethylene triamine and
triethylene tetramine are exemplary; aromatic amines of
30 which methylene dianiline, meta phenylene diamine,
4,4' diaminodiphenyl sulfone are exemplary; and
polycarboxylic acid anhydrides of which pyromellitic
dianhydride, benzophenone tetracarboxylic dianhydride,
hexahydrophthalic anhydride, nadic methyl anhydride
35 (maleic anhydride adduct of methyl cyclopentadiene),

1 methyl tetrahydronaphthalic anhydride and methyl
hexahydronaphthalic anhydride are exemplary. Polycarboxylic
acid anhydride compounds are preferred curing agents
for the above-noted preferred epoxy resins, with the
5 three compounds last noted being most preferred.

In preparing heat curable, thermosetting, epoxy
resins compositions, the epoxy resin is mixed with the
curing agent in proportions from about 0.6 to about 1.0
10 of the stoichiometric proportions, which provides suffi-
cient anhydride groups and carboxylic acid groups to react
with from about 60 to 90 percent of the epoxide groups.
The term "curing" as used herein denotes the conversion
of the thermosetting resin into an insoluble and infusible
15 cross-linked product and, in particular, as a rule,
with simultaneous molding to give shaped articles.

In addition curing accelerators may be added to
the epoxy resins, as is known in the art, to provide a
low curing temperature. Preferred accelerators for the
above-noted preferred polyglycidyl aromatic amine
20 resins are substituted imidazoles, such as 2-ethyl-4-
methyl imidazole, and organometallic compounds, such as
stannous octoate, cobalt octoate, and dibutyl tin
dilauroate which are incorporated at a concentration of
zero to about 3 parts by weight per 100 parts resin.

25 Moreover, other materials may be added to the
epoxy material in order to improve certain properties
thereof, as is known in the art. For example, the
tendency of the resin to separate from the mixture
can be minimized by the addition of fine particulate
30 fillers, such as Cab-O-Sil (a fumed silica manufactured
by Cabot Corporation), acicular fibers, such as talc,
or short chopped or milled fibers. In addition, resin
penetration of the filler may be enhanced by the addition
of a titanate wetting, agent, such as KR38S, an isopropyl
35 tri(dioctylpyrophosphate) titanate, available from
Kenrich Petrochemical Co.

1 A particularly useful resin composition for
forming the composites of the present invention comprises
a polyglycidyl aromatic amine, a polycarboxylic acid
anhydride curing agent, and a curing accelerator.
5 Examples 3 and 4 herein are directed to the use of
this preferred resin formulation in the practice of
the present invention.

2. Hollow Microspheres

10 The syntactic foam composites prepared in accordance
with the present invention contain a relatively uniform
distribution of hollow microspheres. These hollow
microspheres are usually hollow thermoplastic spheres
composed of acrylic-type resins such as polymethyl-
methacrylate, acrylic modified styrene, polyvinylidene
15 chloride or copolymers of styrene and methyl methacrylate;
phenolic resins; or hollow glass, silica or carbon spheres
that are very light in weight and act as a lightweight
filler in the syntactic foam. These microspheres
preferably have a diameter in the range of about 5 to
20 about 200 micrometers. Methods for the production of
these hollow microspheres are well known in the art
and are discussed, for example, by Harry S. Katz and
John V. Milewski in the book entitled, "Handbook of
25 Fillers and Reinforcements for Plastics," Chapter 19:
Hollow Spherical Fillers, Van Nostrand Reinhold, 1978,
the teachings of which are incorporated herein by
reference. Such microspheres are readily available
commercially. These hollow microspheres can be
30 compressed somewhat when subjected to external pressure.

1 However, they are relatively fragile and will collapse
or fracture at high pressures. Therefore, there is a
pressure range under which the microspheres can
effectively operate. It has been determined that when
5 hollow glass microspheres are employed in the practice
of the present invention, syntactic foam composites
can be molded at pressures up to the limit of the
hollow microspheres without fracture, with molding
pressures in the range of about 700 to about 900 psi
10 (0.102 to 0.131 pascals) being preferred.

By controlling the amount of hollow microspheres added to the syntactic foam, it is possible to control the specific gravity of the foam. A simple mixture of an epoxy material and hollow microspheres tends to separate on standing, with the microballoons rising to the surface of the epoxy. However, it has been found that with an increased volume of microballoons added to the epoxy, there is a decreased tendency to separate into discrete phases. Moreover, it has been found that at a sufficiently high loading of microballoons, namely about 65% by volume for microballoons, the tendency to separate into discrete phases is minimized. To achieve specific gravities of less than 1.0, the hollow microspheres are included in the syntactic foam in up to 65% by volume and generally in a range of about 35 to about 65% by volume and preferably about 50 to about 65% by volume. The volume percentage of hollow microspheres is adjusted based on the composition of the hollow microsphere selected, the brand of microspheres and the size of the microspheres. Therefore, it may be necessary to select the proper mixture of heat curable resin material and hollow microspheres for preparation of the syntactic foam on a trial and error basis. For example, the C15/250 series of glass microspheres available from the 3M Company has a specific gravity of 0.15 and a mean diameter of 50 micrometers.

1 "Carbosphere" carbon microspheres available from the
Versar Corporation have a specific gravity of 0.32 and
a mean diameter of 50 micrometers. Desirably, a mixture
of two or more types of hollow microspheres may be
5 employed in the practice of the present invention. The
glass microspheres provide the syntactic foam with
improved structural strength, while those of carbon
advantageously contribute to both a lowered coefficient
of thermal expansion and greater amenability to subsequent
10 metal-plating operations. When using a combination of
glass and carbon microspheres in preparing the composites
of the present invention, the ratio of glass microspheres
to carbon microspheres is about 1:4 to 1:1.

15 Furthermore, it has been found by using packing
theory that an increased volume percent solids in the
resin mixture can be achieved. Packing theory is based
on the concept that, since the largest particle size
filler in a particular reinforcement system packs to
produce the gross volume of the system, the addition of
20 succeedingly smaller particles can be done in such a
way as to simply occupy the voids between the larger
filler without expanding the total volume. This theory
is discussed by Harry S. Katz and John V. Milewski, in
the book entitled "Handbook of Fillers and Reinforcements
25 for Plastics," Chapter 4. Packing Concepts in Utilization
of Filler and Reinforcement Combinations, Van Nostrand
Reinhold, 1978. The fillers used in the present
invention are chosen on the basis of particle size,
shape, and contribution to overall composite properties.
30 This theory applies to the use of solid particulates as
well as hollow spheres. Because of the high viscosity
of such a highly loaded resin, the mixture could not
flow into the mold without damaging the microspheres.

1 To overcome this problem, the mold is pre-packed with
the dry filler (i.e. a mixture of microspheres and
fibers). By applying packing theory as described above,
the filler can be packed at high density and so that
5 segregation of ingredients does not occur.

10 Finally, the microspheres may be advantageously
treated with a coupling and wetting agent to enable the
resin to wet the sphere surfaces and promote good filler-
resin adhesion, as discussed in greater detail below
with regard to similar treatment of the fibers used in
the present invention.

3. Fibers

15 The fibers used in the practice of the present
invention must be compatible with the selected resin in
order to provide good coupling between the fiber and
resin. Fibers such as graphite, glass, Kevlar (an
aromatic polyamide material obtained from E. I. Dupont
and Company) nylon, or carbon are added to the syntactic
20 foam composite of the present invention to improve the
strength and dimensional stability of the composite.
However, the contribution of the fiber to the coefficient
of thermal expansion of the composite product and to
the viscosity of the mixture of components must also
25 be considered. Graphite fibers have been found to be
particularly useful since they provide the desired
strength in the composite, while also reducing the
coefficient of expansion of the composite. An additional
factor to consider is fiber length. While shorter
30 fibers (e.g. having a length-to-diameter ratio of less
than 100:1) provide less reinforcement per fiber than
do longer fibers, shorter fibers have less impact on
the viscosity of the mixture. Thus, a greater volume
fraction of shorter fibers can be incorporated into a

1 mixture at a given level of viscosity, which provides a
higher level of reinforcement at that viscosity level
by shorter fibers. In addition, the use of shorter
fibers improves the uniformity of the mix. Thus,
5 fibers useful in the composite of the present invention
have a length less than or equal to 250 micrometers
and generally in the range of about 50 to about 250
micrometers. Fibers having a length about 150 to
about 250 micrometers were found to provide the best
10 compromise between viscosity and reinforcement as
discussed previously. When graphite fiber, the preferred
fiber material, is used, the diameter of the graphite
fibers is in the range of about 5 to about 10 micrometers.

Moreover, the interaction of the fibers with the
15 microspheres discussed previously must be considered.
It has been determined by micropacking theory, as
described in Chapter 4 of the book by Katz and Milewski,
previously referenced, that the optimum ratio of fibers-
to-spheres varies with the length/diameter ratio (L/D)
20 of the fibers and with the ratio of the sphere-diameter
to the fiber-diameter (R). For each value of L/D ,
there is one R value where the packing efficiency is
zero; and as R increases or decreases on either side of
this minimum, packing efficiency increases. It has
25 been found most desirable in the practice of the present
invention to use graphite fibers of the micrometer
lengths discussed above, which have a length to diameter
ratio (L/D) of about 5:1 to about 30:1 and preferably
about 15:1 to about 30:1, and a sphere-diameter to
30 fiber-diameter ratio (R) of at least about 6:1 and
preferably about 15:1.

Graphite fibers used in the practice of the
present invention are selected to have high strength
and low density. Celanese GY-70 graphite fiber and
35 Courtaulds HM-S graphite fiber are especially suitable.

1 Celanese GY-70 fiber is 8 micrometers in diameter,
has a tensile strength of 76,000 pounds per square inch
(3.6389×10^6 Pa), a specific gravity of 1.83 gm/cm³
and an α of -0.3×10^{-6} in/in/°F. Courtaulds HM-S
5 graphite fibers have a diameter of 8 micrometers, a
tensile strength of 50,000 psi (2.394×10^6 Pa), a
specific gravity of 1.91 gm/cm³ and a longitudinal
 α of -1×10^{-6} in/in/°F. The graphite fibers are
commercially available as continuous-fiber tows. For
10 example, Celanese GY-70 fiber consists of 384 fibers/tow.
The fiber tows are reducible to required lengths on the
order of between about 50 micrometers and 250 micrometers
by ball milling or from commercial processing concerns
such as the Courtaulds Company of the United Kingdom.

15 The amount of fiber incorporated in the resin-
microsphere admixture generally ranges from about 3 to
about 10 volume percent and preferably from about 3 to
about 5 volume percent in order to achieve composites
having α values of 25×10^{-6} in/in/°F (45×10^{-6} cm/cm/°C)
20 or less.

As the amount of hollow microspheres and fibers
incorporated in the heat curable resin increases, there
is a corresponding increase in the viscosity of the
resin. High viscosity prevents uniform dispersion of
25 the microspheres and fibers and interferes with the
processing of the resin-microsphere-fiber mixture during
molding operations. However, in order to reduce the
viscosity of the mixture, the surfaces of the microspheres
and fibers may be provided with a thin layer of coupling
30 and wetting agents. The microsphere and fiber surfaces
are treated with a solution containing a silane coupling
agent such as Silane A-186 (beta(-3,4-epoxy cyclohexyl)-
ethyltrimethoxy silane), Silane A-1120 (n-beta-
(aminoethyl)-gamma-aminopropyl tri-methoxy-silane) or a

1 titanate coupling agent such as di(dioctylpyrophos-
phato)ethylene titanate (KR238M available from Kenrich
Petrochemical Company of Bayonne, New Jersey); or
5 tetra(2,2 diallyloxyethyl-1-butoxy)titanium di(ditridecyl
phosphite) (KR55 available from Kenrich); or titanium
di(cumylphenylate) oxyacetate (KR134S available from
Kenrich); or isopropyl tridodecylbenzenesulfonyl
10 (KR9S available from Kenrich). The coupling agents
enable the resin to wet the sphere and fiber surfaces, and
promote a stronger bond between the resin, microspheres,
15 and fibers without increasing the viscosity appreciably.

The coupling agents may be applied by simply
dissolving the agents in the resin-microsphere-fiber
blend. Optionally, these agents may be applied by
first dissolving the agents at a concentration of
20 0.1 - 0.5% of the filler weight in water or an organic
solvent such as isopropanol or Freon TE (a fluorocarbon
compound available from E.I. Dupont and Company); and
then immersing the microspheres and fibers which have
been premixed in predetermined proportions in the
solution for a period of 5 to 30 minutes, followed by
filtering and drying the mixture. The microsphere-fiber
mixture may then be blended with the heat curable resin
25 preparatory to fabricating the syntactic foam composite.

25

4. Optional Microbeads

Solid microbeads may optionally be incorporated
in the composite of the present invention in order to
increase packing efficiency. Advantageously, such
30 microbeads were also found to decrease the viscosity of
the formulation, improve its pourability, and increase
composite uniformity. In a preferred practice of the
present invention, about 2 to about 8 percent by volume
of solid inert material, such as glass or silica micro-
beads having a diameter of about 2 to about 8 micrometers
35

1 and a specific gravity of 2.2 to 2.4 are incorporated
in the resin-microsphere-fiber admixture. Volume
percentages in excess of 8% increase the viscosity of
the uncured, filled heat curable resin formulation to
5 a level at which it is unworkable for molding purposes.
In addition, it was found that large filler volume
fractions (volume of microballoons, fiber and microbeads
greater than 60 percent) had a reduced coefficient of
thermal expansion, but the viscosity of the mix was
10 unworkable. Small volume fractions of filler (i.e.
volume of microballoons, fiber, and microbeads less
than 40 percent) were found to improve processability,
but increased the coefficient of thermal expansion to
an unacceptable level. However, by choosing a filler
15 combination that maximized filler volume yet minimized
filler surface area, both viscosity and the coefficient
of thermal expansion were reduced. Such a combination
was used in the reinforced syntactic foam RSF-34F shown
in Table III, which was processable, uniform, had good
20 physical properties, and was successfully cast in a
metal mold.

In preparing syntactic foams by the method of the
present invention, the hollow microspheres and graphite
fibers, and optionally the solid microbeads, are admixed
25 with the heat curable resin in any conventional fashion
using a suitable mixing device such as a Waring blender.
The homogeneous admixture is then degassed as by applying
a vacuum. Then the mixture is loaded into a mold of
suitable configuration from a reservoir or by using an
30 air gun or other conventional loading device. The shape
of the mold will, of course, determine the shape of the
cured product and may be chosen as required to form a
desired structure, such as an antenna waveguide. Molding
is then accomplished in an autoclave at the temperature

1 at which the resin is curable, e.g. to 250°F to 350°F
150°F to 250°F (66 to 121°C) for epoxy resins generally and about
150°F to 250°F (66 to 121°C) for the preferred epoxy
composition described herein, at 50 to 100 psi (2586 to
5 5171 mm Hg or 7.25 to 14.5×10^{-3} Pa) for about 2 to
about 4 hours.

Molding of the filled heat curable resin formulations to form syntactic foam composites of the present invention may also be effected by other conventional
10 molding methods including transfer molding and compression molding procedures wherein the heat curable formulation is cured at the above-noted curing temperatures, using pressures on the order of 800 to 1000 psi (41372 to 51715 mm Hg or 0.116 to 0.145 pascals) for 1 to 2 hours.

15 It has been found particularly advantageous to form the filled heat curable resin mixtures into the syntactic foam composites of the present invention by a vacuum liquid transfer molding process. In this procedure, the mold is first loaded with the microsphere/
20 fiber filler which has been mechanically or manually premixed in predetermined proportions and pretreated with a sizing agent as previously described. Next, the mold may optionally be vibrated to promote a uniform distribution of the filler in the mold (e.g. about 5 minutes on a vibration table). Then the mold cavity is filled with the heat curable resin. The mold
25 cavity is a sealable pressure vessel constructed to support the vacuum/pressure sequence described below. To prepare for the molding process, the mold cavity is preheated to bring the cavity up to the temperature at
30 which the heat curable resin is curable. A vacuum is then drawn on the mold to degas the mold cavity contents and to impregnate the filler with the resin. The vacuum is released to atmospheric pressure to

1 burst any gas bubbles remaining in the mold contents.
Then, a superatmospheric pressure, such as 100 to 1000
psi (0.01456 to 0.145 pascals), is applied to the mold
to cause the resin to encapsulate the filler. The
5 elevated temperature and superatmospheric pressure are
maintained for a time sufficient to partially cure the
resin and form a unitary structure which can be ejected
from the mold. The ejected structure is then subjected
to a further heating cycle to completely cure the resin.

10 By the practice of the present invention,
reinforced syntactic foam composites are obtained
which have a coefficient of thermal expansion of about
 25×10^{-6} in/in/ $^{\circ}\text{F}$ (45×10^{-6} cm/cm/ $^{\circ}\text{C}$) or less
and a density of less than 1.0 gm/cm 3 , as well as
15 long-term thermal stability, amenability to being
molded in various configurations, and ability to meet
the NASA outgassing requirements. Using the
preferred epoxy resin formulation described herein,
composites are obtained which have a coefficient of
20 thermal expansion of about 9.0×10^{-6} in/in/ $^{\circ}\text{F}$ (16.2
 $\times 10^{-6}$ cm/cm/ $^{\circ}\text{C}$) or less. In addition, the mechanical
properties of these composites are repeatable.
This combination of properties makes the composites of
the present invention particularly well suited for use
25 as a substitute for aluminum in antenna and antenna
microwave components used in space applications. In
particular, heat curable epoxy resins comprised of
mixtures of tetrafunctional aromatic epoxy resins and
liquid anhydride when heated to 150°F are sufficiently
30 low in viscosity to accept loadings of microspheres up
to 65 percent of the volume of the system, fiber loadings
of up to 10 percent, and bead loadings up to 65 percent.
These microsphere/fiber/bead filled epoxy resins are
readily curable and when cured produce syntactic foam
35 composites having specific gravities of between 0.8 and
0.9 and coefficients of thermal expansion approximating

1 that of aluminum or steel. Depending on the filler
fiber volume used in the composite of the present
invention, composites may be tailored to have coefficients
of thermal expansion ranging from that of the unfilled
5 resin to that of steel.

Because of their relatively low coefficient of
thermal expansion, epoxy resin based syntactic foam
composites prepared in accordance with the present
invention have been determined to be especially amenable
10 to conventional metal plating processes, such as electro-
less plating, when the surfaces thereof are prepared
for plating by plasma treatment. The relatively high
adhesion of metal deposits to the surface of the present
composite is believed to be a function of both the
15 topography of the plasma-treated surface plus the
mechanical integrity of the remaining surface. The
plasma removes the resin "skin" from the composite,
leaving the graphite fiber/microballoon filler exposed,
to provide a surface which is readily platable. Such
20 metal plating of the composite of the present invention
may be required in forming antenna components in which
an electrically conductive surface or path is required,
as is known in the art.

To effect plasma treatment in preparation for
plating, the surface of the filler reinforced epoxy
resin based composite is subjected to a plasma process
with a reaction gas containing a mixture of air, nitrogen,
or argon with oxygen, water vapor, nitrous oxide, or
other resin oxidizing source, to remove the polymer
25 "skin" and expose the filler, as discussed above.
Normal plasma etching conditions known to the art are
used. For example, for a plasma excitation energy of
30 200 watts/ft² of composite, an O₂/inert gas source
of approximately 1000 ml/minute, a vacuum pressure of
35 200 micrometers Hg, and one hour duration are used.

1 When a silver deposit is required, as in an
antenna waveguide structure, it is advantageous to
first form a layer of an electroless or vapor deposited
metal such as copper to provide a conductive surface
5 which can then be built up with additional electrolytic
plating such as copper or silver plate to produce a
smooth surface finish. Electrolytic silver plating may
readily be formed on the electrolytic copper surface to
provide a silver plated surface with good adhesion to
10 the underlying composite material.

Electroless plating of the plasma-treated composite
surface can be accomplished by standard procedures such
as by dipping the plasma-treated composite in the plating
solution for a time sufficient to achieve a continuous
15 buildup of metal on the etched surface. Metals that
can be plated on the molded epoxy resin based composites
prepared in accordance with the present invention
include, for example, copper, silver, nickel, cobalt,
nickel/iron, nickel/cobalt, other nickel alloys, and
20 gold. For electroless copper plating, an aqueous bath
of Shipley Co. #328 copper plating solution may be
used, which contains copper sulfate, sodium potassium
tartrate, and sodium hydroxide. Other electroless
copper plating formulations can also be employed. The
25 plating bath is agitated or stirred prior to immersion
of the plasma-treated composite. Preferred plating
temperatures are in the range of about 15°C to about
95°C (about 59°F to 203°F). Metal adhesion of this
electroless copper plating has been determined to be
30 excellent even after exposure of the plated composite
to cycles of widely different temperatures, as described
in Examples 3 and 4 herein.

1 Next, a copper plating is built up to any desired
thickness on the electroless copper by known electrolytic
plating methods, using commercially available electro-
deposit copper plating solution. Finally an electrolytic
5 silver plate is formed to the desired thickness on the
electrolytic copper plate by known methods, using
commercially available silver plating solution formula-
tions. Silver plating of a composite of the present
invention is described in Example 5.

10

The following examples illustrate but do not limit
the present invention.

15

EXAMPLE 1

This example illustrates a process for forming
one type of fiber-reinforced syntactic foam composite
in accordance with one process embodiment of the present
invention.

20

The components of the syntactic foam formulation
designated "S-61" are shown in Table I. The following
details regarding the components of S-61 apply to Table I.

25

a. MY720 is a tetraglycidyl methylene dianiline
manufactured by Ciba Geigy.

b. HY906 is a nadic methyl anhydride hardener
manufactured by Ciba Geigy.

c. BDMA is benzylidimethylamine accelerator
available from E.V. Roberts or Ciba Geigy.

30

d. D32/4500 microspheres are borosilicate
microspheres having a mean diameter of 75
micrometers, a specific gravity of 0.32, and a
compressive strength of 4500 psi, available from
the 3M Company.

35

- 1 e. GY70 fibers are graphite fibers milled to a
length of about 150 micrometers and having a
diameter of about 8 micrometers, available from
the Celanese Corporation.
- 5 f. KR38S, KR55, and KR9S are titanate coupling
and wetting agents, available from Kenrich
Petrochemical Company, Bayonne, New Jersey.
- 10 g. AF4 is a surfactant, available from Furane
Chemical Co.

10

15

TABLE I
COMPOSITION OF FORMULATION S61

| <u>Component</u> | <u>PHR*</u> | <u>Weight (grams)</u> |
|------------------------------------------------------------------------------------------|---------------------------|--------------------------|
| 20 1. Resin MY720 epoxy resin HY906 hardener BDMA accelerator KR38S | 100 100 0.25 1.0 | 400 1.0 4.0 4.0 |
| 25 2. Microspheres D32/4500 KR55 AF4 (Optional) | 40 0.3 0.2 | 160 1.2 0.8 |
| 30 3. Fibers Milled GY70 KR9S | 20 0.2 | 80 0.8 |

*PHR is parts per hundred epoxy resin

1

Preparation of Graphite Fibers

The GY70 graphite fibers in continuous tow form were cut into lengths of approximately 1/8 inch to 1/2 inch (0.32 to 1.27 centimeters), using a paper cutter. 5 Batches of the chopped fibers (approximately 80 grams each) were loaded into a ball mill jar having a one-gallon capacity and sufficient Freon TF was added to cover the ceramic balls to serve as a suspension medium. The fibers were milled for 24 hours. Scanning electron 10 micrographs of the milled fibers showed them to be broken into small fragments ranging from approximately 2 to 10 micrometers in length.

The milled fibers and Freon were poured into a shallow stainless steel pan, and the Freon was allowed 15 to evaporate. The fibers were then dried 4 hours in an air-circulating oven set at 250°F (121°C) and sifted on a vibration plate to pass a 325 mesh screen. The dried, sifted fibers were stored in a desiccator box until ready for use.

20

Composite Formation

The formulation S61 was prepared as follows. A one-gallon hot/cold pot for a Waring blender was heated 25 to 140°F (60°C) using a temperature-controlled water bath. The premeasured amount of the HY906 hardener was put in the blender and the mixer speed was adjusted using a Variac variable potentiometer so that the hardener was just barely agitated. With the blender on "low" setting, the Variac was turned to 70 percent of 30 full speed. The resin, which had been preheated to 160°F (71°C), was added to the pot and the contents of the pot were mixed until the mixture appeared homogeneous (about 5 minutes), and then cooled to room temperature.

1 Next, there was gradually added to the pot the KR38S,
AF4 (optional), and 25 percent of the milled fibers
which had been previously dried overnight in an oven at
200°F (93°C) and fluffed by running in the blender on
5 "low" speed at 70 percent of the full Variac speed for
about 15 seconds for 5 grams of fiber. The mixture was
mixed for about 5 minutes. Next, 10 percent of the
microspheres which had been dried overnight in an oven
at 200°F (93°C) was gradually added and the contents of
10 the pot were mixed until streaks of microspheres disap-
peared. The remaining amount of fiber and the KR9S
were gradually added and the pot contents mixed for
about 30 minutes. Next, the BDMA was added slowly,
followed by the KR55 and the remaining amount of micro-
15 spheres. The pot contents were mixed until streaks of
microspheres disappeared.

Then, the pot was covered and a vacuum pump was
attached to the pot with the pump set to pull a vacuum
of 22 inches (559 mm) of mercury. The mixer was run
20 for 45 minutes under vacuum or until there were no
black streaks of fibers in the mixture. Finally, the
mixture was carefully poured so as to minimize air
entrapment, into a preheated stainless steel test
specimen mold which had been prepared by: cleaning
25 with methyl ethyl ketone solvent, baking at 300°F (149°C)
for 30 minutes, brushing with a fluorocarbon mold
release agent to provide three coats of the release
agent with 30 minutes air drying for each coat, and
preheating to 140°F (60°C). (Optionally, the formulation
30 was injected with an air gun into the mold.) After
pouring the mixture into the mold, the mold was vibrated
on a vibrating table for 5 minutes at the maximum safe
speed, with a large, flat, 0.5 inch thick aluminum
plate placed on top of the mold. Next, the mold was

1 placed in an oven preheated to 275°F (135°C) and a
thermocouple was placed on/in each of the following: on
the mold, in the oven, and in the mold contents through
a hole in the side wall of the mold. When the thermo-
couple in the mold contents registered 275°F (135°C),
5 the following cure cycle was run: 10 minutes at 275°F
(135°C); 10 minutes at 300°F (149°C); 120 minutes at
350°F (177°C). The maximum oven rate was used for
changing temperatures.

10 The mold was removed from the oven and was
disassembled, and the part was removed from the mold
while the mold was still hot, being sure to keep the
thermocouple embedded in the syntactic foam. The part
was deflashed as necessary with a file. For the post-
cure, the demolded part was placed in an oven preheated
15 to 400°F (204°C) between 0.5 inch thick aluminum plates,
with 2-5 kilograms weight on the top plate. When the
thermocouple in the syntactic foam registered 400°F
(204°C), the following post-cure cycle was run: 1 hour
at 400°F (204°C); 1 hour at 425°F (218°C); 1 hour at
20 450°F (232°C), and 1 hour at 475°F (246°C) Finally, the
part was removed from the oven.

25 The fiber reinforced syntactic foam composite
formed as described above was found to have the properties
shown in Table II. With regard to Table II, the
following test requirements apply:

- a. CTE was determined using a quartz
dilatometer to measure the change in
length as a function of temperature.
- b. Specific gravity was measured using a
pycnometer.
- c. Viscosity was measured with a Brookfield
Viscometer.

- 1 d. Shrinkage was measured by determining the dimensional difference between the molded product and the mold.
- 5 e. Gel time was determined qualitatively as the time required for the liquid resin to form a gel.
- 10 f. Pot life was determined qualitatively as the time required for the liquid resin to increase in viscosity to the point of being unworkable.
- 15 g. Degree of exotherm was determined by using a differential scanning calorimeter.

15

TABLE II
PROPERTIES OF COMPOSITE OF S61 FORMULATION

20

| Property | Value |
|-----------------------------|----------------------------------------------------------------------------------------------|
| CTE | $19-22 \times 10^{-6}$ cm/cm/ $^{\circ}$ C $10.6-12.7 \times 10^{-6}$ in/in/ $^{\circ}$ F |
| Specific gravity | 0.80 |
| Viscosity at 150°F (65.6°C) | 35,000 centipoise |
| Shrinkage | 0.8% |
| Gel time | >60 minutes |
| Pot life | >360 minutes |
| Degree of exotherm | 15°F (8.3°C) |

EXAMPLE 2

1 This example illustrates a process for forming
fiber-reinforced syntactic foam composites of various
compositions in accordance with the present invention.

5 The components of the various formulations
designated as the "RSF series" are shown in Table III.
The following details regarding the specific components
apply to Table III.

- a. Epoxy is a mixture of 70 parts Glyamine 135
(diglycidyl ortho toluidine) and 30 parts
Glyamine 120 (tetraglycidyl methylene
dianiline), both materials obtained from FIC
Resins of San Francisco, California, mixed
with about 115 parts nadic methyl anhydride
hardener and about 0.25 parts benzylidimethyl-
aniline accelerator.
- b. Zeeospheres 0/8 are solid glass spheres
having a median diameter of 3 micrometers,
available from Zeelan Industries of St. Paul,
Minnesota.
- c. Carbospheres Type A are hollow carbon spheres
having an average diameter of 50 micrometers,
available from Versar of Springfield, Virginia.
- d. 3M A 32/2500 glass bubbles are glass micro-
spheres having a mean diameter of 50 micro-
meters, a specific gravity of 0.32, and a
compressive strength of 2500 psi, available
from the 3M Company of Minnesota.
- e. 3M A 16/500 are glass microspheres having a
mean diameter of 75 micrometers, a specific
gravity of 0.16, and a compressive strength
of 500 psi, available from the 3M Company.
- f. Eccospheres SI are hollow silica microspheres
having a diameter of 45-125 micrometers,
available from Emerson and Cuming Inc. of
Canton, Massachusetts.

- 1 g. Grefco 213 R40 beads are solid glass micro-
 spheres having a diameter of 3-8 micrometers,
 available from Grefco Inc. of Torrance,
 California.
- 5 h. HM-S 50 (50μ) are graphite fibers having a
 length of about 50 micrometers and a diameter
 of about 8 micrometers, available from
 Courtaulds Co. of the United Kingdom.
- 10 i. AS 50 (250μ) graphite are graphite fibers
 having a length of about 250 micrometers and
 a diameter of about 8 micrometers, available
 from Courtaulds of the United Kingdom.
- 15 j. 0.063" HMS-50 (1/16") are graphite fibers
 having a length of about 1600 micrometers
 and a diameter of about 8 micrometers,
 available Finn and Fram of Sun Valley,
 California.

Using each of the formulations of the RSF series
20 designated in Table III, a fiber-reinforced syntactic
foam composite was formed following the general procedure
set forth in Example 1. The properties of each of
these composites is shown in Table IV. The following
test requirements were applied for the measurements in
25 Table IV.

- 1 a. Density was determined by pycnometer.
- 5 b. CTE was determined using a quartz dilatometer to measure the change in length (Δl) as a function of temperature.
- 10 c. Compressive strength was determined using the American Society for Testing and Materials (ASTM) Standard No. D695.
- 15 d. Compressive modulus was determined using ASTM D695, using crosshead speed in place of strain guages.
- 20 e. Uniformity was determined by visual inspection.
- 25 f. Viscosity was measured with a Brookfield Viscometer.

15

20

25

30

35

TABLE III
COMPOSITION OF FORMULATIONS OF RSF SERIES

| RSF- FORMULATION | EPOXY | VOLUME RATIO OF FOAM FILLERS | | | | | |
|---------------------|-------|------------------------------|------------------------|------------------------------|-------------------|-----------------------------|----------------------------------|
| | | MICROSpheres | | | FIBERS | | |
| | | ZEEOSPHERES 0/8 | CARBOSPHERES TYPE A | 3M A32/2500 GLASS BUBBLES | ECCOSPHERES SI | GREFCO 213 R 40 BEADS | HM-S 50 _μ GRAPHITE |
| 3 | 0.405 | 0.098 | | 0.471 | | 0.025 | |
| 4 | 0.375 | 0.048 | | 0.514 | | 0.064 | |
| 5 | 0.401 | | | 0.500 | | 0.040 | |
| 6 | 0.401 | | | 0.500 | | 0.034* | |
| 7 | 0.536 | 0.057 | | 0.400 | | | |
| 8 | 0.530 | 0.057 | | 0.395 | | | |
| 13 | 0.536 | 0.057 | | 0.400 | | | |
| 14 | 0.530 | 0.057 | | 0.395 | | | |
| 19 | 0.37 | 0.05 | | 0.51 | | | |
| 20 | 0.322 | 0.041 | | | | 0.007 | |
| 21 | 0.375 | 0.048 | | | | 0.018 | |
| 23 | 0.583 | 0.023 | 0.368 | | | | |
| 25 | 0.503 | 0.022 | 0.450 | | | | |
| 26 | 0.583 | 0.023 | 0.368 | | | | |
| 28 | 0.583 | 0.023 | 0.368 | | | | |
| 29 | 0.583 | 0.023 | 0.368 | | | | |
| 31 | 0.496 | 0.022 | | 0.457 | | | |
| 33 | 0.503 | 0.022 | | | | 0.025 | |
| 34 | 0.394 | 0.026 | | 0.550 | | 0.025 | |
| 34F | 0.410 | 0.025 | | 0.530 | | 0.030 | |
| 35 | 0.353 | 0.028 | | 0.588** | | 0.035 | |
| 36 | 0.383 | 0.026 | | | | 0.032 | |
| | | | | | | 0.031 | |

* Plus 0.007 of AS 50 (250) graphite

** 3M A16/500 used in place of A32/2500

TABLE IV
PROPERTIES OF COMPOSITES OF FORMULATIONS OF RSF SERIES

| RSF- FORMULATION | DENSITY (g/cc) | CTE (10 ⁻⁶ in/in/°F) | COMPRESSIVE STRENGTH (psi)* | COMPRESSIVE MODULUS (10 ³ psi)* | UNIFORMITY (1-10) | VISCOSEITY |
|---------------------|-------------------|------------------------------------|-----------------------------------|--------------------------------------------------|----------------------|------------|
| 3 | 0.898 | 16.82 | 15,300 | 394 | 3.7 | 5 |
| 4 | 0.881 | 13.81 | 16,300 | 447 | 4.3 | 4 |
| 5 | 0.872 | 15.10 | 16,400 | 406 | 4.0 | 4 |
| 6 | 0.869 | 22.16 | 14,300 | 407 | 3.5 | 5 |
| 7 | 0.968 | 20.82 | 15,100 | 394 | 2.7 | 8 |
| 8 | 0.982 | 21.39 | 18,400 | 410 | 4.7 | 7 |
| 13 | 1.000 | 25.46 | 14,900 | 386 | 2.3 | 7 |
| 14 | 1.019 | 25.55 | 15,400 | 405 | 1.8 | 6 |
| 19 | 0.852 | 14.06 | 13,200 | 411 | 4.0 | 3 |
| 20 | 0.694 | 14.09 | 8,600 | 335 | 2.7 | 2 |
| 21 | 0.8561 | 17.02 | 14,000 | 439 | 3.4 | 3 |
| 23 | 0.9912 | 20.69 | 16,300 | 384 | 5.5 | 7 |
| 25 | 1.0387 | 30.51 | 19,000 | 423 | -- | 6 |
| 26 | 1.005 | 21.73 | 15,700 | 395 | 7.3 | 5 |
| 28 | 0.982 | 20.10 | 17,100 | 411 | 6.5 | 5 |
| 29 | 1.002 | 20.70 | 17,800 | 393 | 7.6 | 5 |
| 31 | 0.888 | 23.90 | 17,800 | 400 | 6.6 | 8 |
| 33 | 0.815 | 23.10 | 13,300 | 343 | 3.9 | 7 |
| 34 | 0.824 | 14.59 | 17,500 | 394 | 4.4 | 6 |
| 34F | 0.842 | 14.24 | 17,300 | 425 | -- | -- |
| 35 | 0.738 | 17.23 | 10,200 | 303 | 4.0 | 6 |
| 36 | 0.745 | 17.14 | 12,100 | 335 | 3.0 | 5 |

* 1 psi = 1.45 x 10⁻⁴ pascals

1

EXAMPLE 3

5

This example illustrates the formation of a fiber-reinforced syntactic foam composite using the preferred epoxy resin formulation and preferred vacuum liquid transfer molding process described herein.

The heat curable epoxy resin formulation had the following composition:

10

| <u>Resin Component</u> | <u>WT. (gms.)</u> |
|------------------------|-------------------|
|------------------------|-------------------|

| | |
|----------------------------|-----|
| Diglycidyl orthotoluidine | 100 |
| Nadic methylanhydride | 100 |
| 2-ethyl-4-methyl imidazole | 2 |

15

This composition had a gel time of 25 minutes, a viscosity of 220 centipoise at 75°F (24°C), and a CTE of 30.8 to 32.3×10^{-6} in/in/°F (55.8 to 58.1×10^{-6} cm/cm/°C).

20

A filler mixture was prepared having the composition shown below and a density of 0.543 gm/cm³. Carbospheres are hollow carbon microballoons having a mean diameter of about 50 micrometers, available from Versar Inc. of Springfield, Virginia. HM-S graphite fibers are graphite fibers having a length of about 50 micrometers, available from Courtaulds Co. of the United Kingdom. Titanate sizing agents are available from Kenrich Petrochemical Co. of Bayonne, New Jersey.

30

35

| | <u>Filler Component</u> | <u>WT. (gms.)</u> |
|---|---------------------------------|-------------------|
| | Carbosphere, 50 micrometers | 50 |
| | HM-S fiber, 50 micrometers | 50 |
| 5 | Titanate sizing agent KR238M | 1 |

Using the above-noted resin and filler, each of a series of resin/filler formulations shown in Table V was processed as described below in order to form the composite of the present invention.

The filler composition (i.e. a mixture of the fibers and microspheres pretreated with the sizing agent as previously described herein) was loaded into a cleaned 5.5 inch x 0.5 inch (14cm x 1.3cm) wide slab mold internally coated with a polyvinyl alcohol release agent. The mold was preheated to 212°F (100°C), the temperature at which hardening of the heat curable epoxy resin formulation was initiated. The epoxy resin formulation was poured into the mold containing the filler. The mold was placed in a laminating press, a nylon vacuum bag was constructed around the compression tooling of the press, and a vacuum pressure of 125 millimeters (mm) mercury pressure (166,625 pascals) was maintained on the assembly for 2 minutes to draw down the resin to impregnate the filler and to degas the resin materials in the mold. The vacuum was then released without removal of the vacuum bag and the assembly held in this passive vacuum state for an additional 2 minutes. Thereafter, a constant positive pressure of approximately 800 pounds per square inch (41,360 mm Hg or 5.5×10^6 pascals) was imposed on the resin/filler mixture in the mold for 2 hours at 212°F (100°C). During this pressurization stage, the resin was bled from the mold in the amount noted in Table V.

1 The molded composite slab had sufficient green strength
to be ejected from the mold, whereafter it was post
cured for 4 hours unrestrained, in an oven set at 300°F
(149°C). The final void-free slab contained the filler
5 ratio noted in Table V and was cut into appropriate
shapes for physical testing. The composite was found
to have the physical properties which are summarized in
Table VI. As indicated by the values for CTE given in
Table VI, unexpected significant improvement in the CTE
10 of these composites was obtained using the preferred
resin composition and filler compositions described
herein.

15 In addition, a typical sample was tested in
accordance with ASTM E-595-77 and found to have a
collected volatile condensable material (CVCM) of less
than 0.1 percent and a total mass loss (TML) of less
than 1 percent, which meets the NASA outgassing
requirements.

20 Further, for Specimen 1 of Table V, a portion
of the molded slab was surface plated with copper by
subjecting the surface of the slab to an oxygen rich
plasma treatment, as previously described. The treated
slab was then dipped into Shipley #328, electroless
copper plating solution, as previously described, and
25 then dried at 248°F (120°C) under 29 inches (737mm) Hg
(guage pressure).

30 The plated composite was then evaluated for
adhesion of the deposited copper layer using an ASTM
D3359 tape adhesion test before and after 25 cycles of
thermal shock imposed on the plated surface by alternately
dipping the plated specimen in liquid nitrogen (-320°F
or -196°C) for 30 seconds and boiling water (212°F or
100°C) for 10 seconds. No loss of copper was observed.

TABLE V
COMPONENTS OF MOLDING COMPOSITION

| Specimen No. | Resin (gms.) | Filler (gms.) | Filler Ratio | | Resin Bleed During Molding % |
|--------------|--------------|---------------|--------------|---------|------------------------------|
| | | | (Wt.%) | (Vol.%) | |
| 1 | 40 | 10 | 45 | 64 | 69.2 |
| 2 | 30 | 9.4 | 38 | 57 | 47.8 |
| 3 | 30 | 9.4 | 38 | 57 | 47.9 |
| 4 | 17.0* | 5.5 | 37 | 57 | 45.3 |
| 5 | 19.0* | 6.0 | 39 | 59 | 50.6 |
| 6 | 20.7* | 6.5 | 41 | 60 | 54.6 |

* KR134S sizing agent was substituted for the previously noted sizing agent.

$$** \text{ Resin bleed} = \left(\frac{W_1 - W_2}{W_1} \right) 100$$

where W_1 = initial resin weight

W_2 = resin displaced from the mold, using a bleeder cloth.

Vol. % calculated from resin bleed varies about 10-20% of the actual vol. % value.

TABLE VI
PHYSICAL PROPERTIES OF MOLDED COMPOSITES

| Specimen No. | Thickness (in.) | Density gm/cm ³ | CTE* 10^{-6} cm/cm/°C (10^{-6} in/in/°F) |
|--------------|-----------------|----------------------------|-----------------------------------------------------|
| 1 | 0.478 | 0.743 | 6.6 (3.6) |
| 2 | 0.550 | 0.900 | 16.2 (9.0) |
| 3 | 0.565 | 0.876 | 14.2 (8.1) |
| 4 | 1.070 | 0.889 | -- |
| 5 | 1.042 | 0.915 | -- |
| 6 | 1.065 | 0.914 | -- |

* Determined using a quartz dilatometer.

EXAMPLE 4

1 This example illustrates the formation of composites
as set forth in Example 3 with the exception that the
composition of the filler formulation was varied. The
5 procedure set forth in Example 3 was followed except
that the filler compositions shown in Table VII were
used. The following details regarding the specific
components apply to Table VII.

- 10 a. Carbospheres are carbon microspheres having
 a specific gravity of 0.32 and a mean diameter
 of 50 micrometers, available from Versar
 Corporation.
- 15 b. HM-S 50 (50 μ) graphite fibers are graphite
 fibers having a length of about 50 micrometers
 and a diameter of about 8 micrometers, available
 from the Courtaulds Co. of the United Kingdom.
- 20 c. 1/4 mm HM-S 50 graphite fibers are graphite
 fibers having a length of about 250 micrometers
 and a diameter of about 8 micrometers,
 available from the Courtaulds Co. of the
 United Kingdom.
- 25 d. C15/250 glass microballoons are composed of
 borosilicate glass, have a diameter of 10-200
 micrometers, a density of 0.15 gm/cm³, and
 a compressive strength of 250 psi, available
 from the 3M Company of Minnesota.

30 The physical properties of the molded composite
 slabs so formed are set forth in Table VIII.

TABLE VII
COMPOSITION OF FILLER FORMULATIONS

| Filler No. | Density (gm/cm ³) | Carbosphere Microballoons (gms) | HM-S 50 (50μ) graphite fiber (gms) | C15/250 glass micro-balloons (gms) | | Titannate Sizing Agent | |
|------------|-------------------------------|---------------------------------|------------------------------------|------------------------------------|--------------|------------------------|-----|
| | | | | 1/4mm HM-S 50 graphite fiber (gms) | KR238M (gms) | KR55 (gms) | |
| A | 0.543 | 50 | 50 | -- | -- | 1 | -- |
| B | 0.328 | 20 | 15 | -- | 10 | -- | 0.5 |
| C | 0.387 | -- | 4.4 | 45.6 | 25 | 1 | -- |

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TABLE VIII
PHYSICAL PROPERTIES OF MOLDED COMPOSITE SLABS

| 5 Filler Used in Molded Sample | Thickness (in.) | Density (gm/cm ³) | Filler Ratio (Wt.%) | Filler Ratio (Vol.%) | Resin Bleed % | Cu Coating Removed |
|--------------------------------------------|--------------------|----------------------------------|------------------------|-------------------------|---------------------|--------------------------|
| A | 0.443 | 1.050 | 39 | 59 | 51.0 | ≤ 5% |
| B | 0.540 | 0.753 | 26-47 | 56-77 | 61.9 | ≤ 5% |
| C | 0.850 | 0.948 | 27 | 54 | 16.2 | 5-15% |

15 In addition, the surfaces of the molded composite slabs of Table VIII were then subjected to plasma treatment under the following conditions: O₂/inert gas source of approximately 1000 ml/minute, vacuum pressure of 200 μ Hg, and one hour duration. The surfaces of the 20 plasma etched slabs were then copper plated to a thickness of about 3-4 mils by dipping the etched slabs in an aqueous Shipley #328 electroless copper plating bath.

25 The plated composite was then evaluated for adhesion of the deposited copper layer using the ASTM D3359 tape adhesion test and thermal shock cycle of Example 3. The adhesion results are recorded in Table VIII, indicating the amount of copper coating on lattice removed by the tape.

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EXAMPLE 5

A syntactic foam composite prepared from Specimen No. 2 of Table V described in Example 3 and molded in a slab mold was plated with silver as follows. The 5 surface of the slab was subjected to an oxygen rich plasma etch which resulted in the removal of the surface polymer "skin," as previously described. The etched slab was then metallized using the Shipley Company #328 electroless copper plating solution process, as 10 previously described, and thoroughly rinsed and dried at 248°F (120°C) under 29 inches (725 mm) Hg (gauge pressure), to provide a layer of electroless copper 20 microinches (5.08×10^{-5} cm) thick. Next, the slab was immersed in an acid copper electrolytic plating 15 bath at 25°C for 25 minutes to form an electrodeposited copper layer 100 microinches (2.54×10^{-4} cm) thick. Finally, the copper-plated slab was immersed in an 20 electrolytic silver plating bath at 25°C for 25 minutes to form a layer of silver 300 microinches (7.62×10^{-4} cm) thick.

The silver-plated slab was then evaluated for adhesion of the deposited layer using an ASTM D3359 tape adhesion test before and after 25 cycles of thermal shock imposed on the plated surface by alternately 25 dipping the plated specimen in liquid nitrogen (-328°F or -196°C) for one minute and boiling water (212°F or 100°C) for one minute. No adhesion loss of silver was observed.

The silver-plated syntactic foam had the same low 30 R.F. loss characteristics as aluminum when tested for insertion loss at 4.6 gigahertz using standard electronic tests. Thus, with the use of proper tooling for molding, antenna waveguide structures may be formed from the 35 composite of the present invention, which are effective microwave or antenna components and which meet the

1 requirements for use in space applications. Syntactic
foams plated with metals such as silver and copper may
serve as metal-plated core materials for both microwave
components and microwave reflectors.

5 The fiber-reinforced syntactic foam composites of
the present invention achieve a 3-to-1 reduction in
weight in comparison with aluminum, which makes these
components attractive for weight-sensitive applications
in a spacecraft environment. At the same time, however,
10 in situations calling for high volume production, the
readily-moldable nature of the reinforced foam mixture
disclosed herein further offers the potential of signifi-
cantly reduced cost in comparison with the machining
traditionally employed for the production of conventional
15 metal parts.

The preceding description has presented in detail
exemplary preferred ways in which the concepts of the
present invention may be applied. Those skilled in the
art will recognize that numerous alternatives encompassing
20 many variations may readily be employed without departing
from the intention and scope of the invention set forth
in the appended claims. In particular, the present
invention is not limited to the specific resin, fibers,
or microballoons set forth herein as examples. By
25 following the teachings provided herein relating to the
effect of each component of the mixture on the final
composite and the effect of the various components on
each other, other suitable resin, fiber, and microballoon
materials may readily be determined. Further, by
30 following the teachings provided herein, it may be
determined how to form composite materials having a
density or coefficient of thermal expansion other than
those set forth herein as required for the specifically
mentioned end use in space applications.

CLAIMSWhat is Claimed is:

- 1 1. A fiber-reinforced syntactic foam composite having a specific gravity less than 1.0 and a coefficient of thermal expansion of about 25×10^{-6} in/in/ $^{\circ}\text{F}$ (45×10^{-6} cm/cm/ $^{\circ}\text{C}$) or less, the composite being prepared from an admixture comprising a heat curable thermosetting resin, hollow microspheres having a diameter in the range of about 5 to about 200 micrometers and fibers having a length less than or equal to 250 micrometers.
- 1 2. The composite of Claim 1 wherein the resin comprises a material selected from the group consisting of an epoxy, a polyester and a condensate of formaldehyde.
- 1 3. The composite of Claim 2 wherein the heat curable thermosetting resin comprises a mixture of an epoxy resin and a polyfunctional curing agent.
- 1 4. The composite of Claim 3 wherein the epoxy resin is tetraglycidyl methylene dianiline, a mixture of diglycidyl orthotolididine and tetraglycidyl methylene dianiline, the diglycidyl ether of Bisphenol A, or a phenol formaldehyde novolac polyglycidyl ether.

1 5. The composite of Claim 3 wherein the polyfunctional curing agent is a polyamine, a polycarboxylic acid anhydride, or the maleic anhydride adduct of methyl cyclopentadiene.

1 6. The composite of Claim 3 wherein the mixture further comprises benzylidimethylaniline as an accelerator.

1 7. The composite of Claim 1 wherein the hollow microspheres are formed of glass, silica, carbon, acrylate resins, or phenolic resins.

1 8. The composite of Claim 7 wherein the hollow microspheres are formed of glass and have an average diameter of about 50 micrometers.

1 9. The composite of Claim 7 wherein the hollow microspheres comprise a mixture of glass microspheres and carbon microspheres.

1 10. The composite of Claim 1 wherein the fibers are formed of graphite, glass, carbon, nylon, or polyamide.

1 11. The composite of Claim 10 wherein the fibers are formed of graphite and have a length of about 50 micrometers and a diameter of about 8 micrometers.

1 12. The composite of Claim 1 wherein said admixture
further includes a coupling and wetting agent.

1 13. The composite of Claim 1 wherein the admixture
further includes solid microbeads.

1 14. The composite of Claim 1 which comprises
about 35 to about 65 percent by volume microspheres
and about 3 to about 10 percent by volume fibers, the
balance being a matrix comprised of the heat cured
5 resin throughout which the microspheres and fibers are
dispersed and bonded together.

1 15. The composite of Claim 14 which additionally
comprises about 2 to about 8 percent by volume of solid
microbeads having a diameter of about 2 to about 8
micrometers.

1 16. A fiber-reinforced syntactic foam composite
as set forth in Claim 1, wherein said heat curable
thermosetting resin comprises an uncured polyglycidyl
aromatic amine, a polycarboxylic acid anhydride curing
5 agent, and a curing accelerator selected from the
group consisting of substituted imidazole compounds
and organometallic compounds, and said composite has a
specific gravity less than 1.0 and a coefficient of
thermal expansion of about 9.0×10^{-6} in/in/ $^{\circ}\text{F}$
10 (16.2×10^{-6} cm/cm/ $^{\circ}\text{C}$) or less.

1 17. The composite of Claim 16 wherein the
polyglycidyl aromatic amine is diglycidylaniline,
diglycidyl orthotolidine, or tetraglycidyl
metaxylylene diamine.

1 18. The composite of Claim 16 wherein the
polycarboxylic acid anhydride is present in sufficient
quantity to react with from about 60 to about 90 percent
of the epoxide groups in said polyglycidyl aromatic
5 amine.

1 19. The composite of Claim 16 wherein the
polycarboxylic acid anhydride is nadic methyl anhydride,
methyl tetrahydrophthalic anhydride, or methyl
hexahydrophthalic anhydride.

1 20. The composite of Claim 16 wherein said curing
accelerator is present in the amount of about 0 to
about 3 percent, by weight.

1 21. The composite of Claim 16 wherein said curing
accelerator is 2-ethyl-4-methyl imidazole or stannous
octoate.

1 22. The composite of Claim 16 wherein:
5 a) said uncured polyglycidyl aromatic amine
is diglycidyl orthotoluidine and is present in the
amount of about 100 parts per hundred resin by weight;
5 b) said curing agent is nadic methyl anhydride
and is present in the amount of about 100 parts per
hundred resin by weight; and
10 c) said curing accelerator is 2-ethyl-4-
methyl imidazole and is present in the amount of about
2 parts per hundred resin by weight.

1 23. A fiber-reinforced syntactic foam composite
as set forth in Claim 16, comprising:

5 a) a heat curable thermosetting epoxy resin
comprising:

- 1) diglycidyl orthotoluidine in the amount of about 100 parts per hundred resin by weight;
- 2) nadic methyl anhydride in the amount of about 100 parts per hundred resin by weight; and
- 3) 2-ethyl-4-methyl imidazole in the amount of about 2 parts per hundred resin by weight;

10 b) hollow carbon microspheres having a diameter in the range of about 20 to about 200 micrometers; and

15 c) graphite fibers having a length of less than or equal to 250 micrometers and a diameter of about 8 micrometers.

1 24. The composite of Claim 1 wherein:

5 a) the heat curable thermosetting resin comprises a mixture of diglycidyl orthotoluidene, tetraglycidyl methylene dianiline, nadic methyl anhydride, and benzylidimethylaniline;

10 b) the hollow microspheres are glass microspheres having a mean diameter of 50 micrometers;

15 c) the fibers are graphite fibers having a length of about 50 micrometers and a diameter of about 8 micrometers; and

20 d) the admixture further comprises solid glass microbeads having a median diameter of 3 micrometers.

1 25. A fiber-reinforced syntactic foam composite
as set forth in Claim 1, comprising:

- 5 a) a heat curable thermosetting epoxy
resin comprising a mixture of tetraglycidyl methylene
dianiline, nadic methyl anhydride, and benzylidimethyl-
aniline;
- 10 b) hollow glass microspheres having a mean
diameter of about 75 micrometers; and
- 10 c) graphite fibers having a length of about
150 micrometers and a diameter of about 8 micrometers.

1 26. An article of manufacture comprising a body
formed from the composite material of Claim 1.

1 27. The article of manufacture set forth in Claim
26 which further comprises a layer of electrically
conductive material adhered to selected surfaces of the
body.

1 28. The article of manufacture set forth in Claim
27 wherein said article comprises a component in an
antenna structure.

1 29. A method for fabricating a fiber-reinforced
syntactic foam composite as set forth in Claims 1-25,
which comprises the steps of:

- 5 a) admixing a heat curable thermosetting
resin, hollow microspheres having a diameter in the
range of about 5 to about 200 micrometers and fibers
having a length less than or equal to 250 micrometers
to form a mixture of the resin, microspheres and fibers;
and

10 b) curing the mixture of the resin, microspheres, and fibers in a mold of predetermined geometry to a thermoset state to provide a composite structure containing about 35 to about 65 volume percent microspheres and about 3 to about 10 volume percent
15 fibers dispersed throughout the resin matrix, and the resin comprising the balance of the composite, wherein the composite has a specific gravity of less than 1.0 and a coefficient of thermal expansion of about 13×10^{-6} in/in/ $^{\circ}$ F (23×10^{-6} cm/cm/ $^{\circ}$ C) or less.

1 30. The method of Claim 29 wherein the admixing comprises:

- a) forming a liquid dispersion of the microspheres and fibers in a coupling agent;
- 5 b) filtering the dispersion to separate the microspheres and fibers from the liquid as a filtration residue;
- c) drying the residue to provide a mixture of microspheres and fibers coated with the coupling agent; and
- 10 d) admixing the coated microspheres and fibers with the resin.

1 31. The method of Claim 30 wherein:

- a) the microspheres are hollow glass microspheres;
- b) the fibers are graphite fibers;
- 5 c) the coupling agent is selected from the group consisting of a silane compound and a titanate compound.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 85/00625

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: C 08 J 9/32; C 08 L 63/00; H 01 Q 15/14; C 08 K 7/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

| Classification System | Classification Symbols |
|-----------------------|--------------------------------------|
| IPC ⁴ | C 08 J; C 08 K C 08 L; H 01 Q; |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

| Category * | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| A | GB, A, 2058794, (NITTA BERUTO) 15 April 1981, see claims; page 1, lines 53-85; examples | 1,2,7,10,12, 26, 29 |
| A | CA, A, 1063747 (J.D.L. TESSIER et al.) 2 October 1979, see claims 1,4; page 4a - page 5, line 2 | 1,2,7,10,12, 26,29 |
| A | Chemical Abstracts, Volume 89, part 2, 10 July 1978, (Columbus, Ohio, US) see abstract No. 89=7325F & JP, A, 7818647 (SUMITOMO ELECTRIC IN- DUSTRIES) | 1-3,5,7,10, 12,26,29 |
| A | GB, A, 1271298 (CIBA-GEIGY) 19 April 1972, see claims 1-8; page 2, lines 50-79; examples I, II; pages 35-124 | 1 |
| A | FR, A, 2112215 (GRUNZWEIG & HARTMANN) 16 June 1972, see claims 1,2,4,5 | 26,27,28 |
| A | EP, A, 0102335 (KEMANORD) 7 March 1984, | |

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

1th July 1985

Date of Mailing of this International Search Report

17 JUL. 1985

International Searching Authority

EUROPEAN PATENT OFFICE

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G.L.M. Knudsenberga

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
|----------|------------------------------------------------------------------------------------|-----------------------|
| | see claims | 1,2,7,13,26, 29,30 |

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 85/00625 (SA 9453)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/07/85

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| EP-A- 0102335 | 07/03/84 | SE-A- 8204595 JP-A- 59047236 US-A- 4483889 | 06/02/84 16/03/84 20/11/84 |

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